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(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To improve reliability of a lithium secondary battery and improve densification of high energy by using carbonaceous powder having a plural-layer structure that a surface layer of a carbonaceous material is formed by baking it under a specific condition after a surface of its nucleus is covered with a carbon precursor by using graphite powder having a specific property as a nucleus, as a negative electrode active material.

SOLUTION: Massive graphite powder has the following characteristic. Spacing of a (002) surface is less than 3.37 Å, and the size of a C axis directional crystallite is not less than 1000 Å, and the ratio of peak intensity of 1360 cm⁻¹ to peak intensity of 1580 cm⁻¹ of a spectrum is not more than 0.3, and a half value width of a 1580 cm⁻¹ peak is not more than 24 cm⁻¹, and the average particle size is 10 to 30 µm, and a thickness of the thinnest part is 3 µm to the average particle diameter, and the specific surface area is 3.5 m²/g to 10.0 m²/g, and tapping density is 0.5 g/cc to 1.0 g/cc, and the X-ray diffraction peak intensity ratio of (110)/(004) is not less than 0.015. Baking to obtain a plural-layer carbonaceous material is performed in a temperature range of 700 to 2800°C in an inert gas atmosphere.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to a nonaqueous electrolyte rechargeable battery, especially relates to the carbon material for negative electrodes of a rechargeable lithium-ion battery.

[0002]

[Description of the Prior Art] Conventionally, as a nonaqueous electrolyte rechargeable battery, it aims at high-energy density-ization by the high voltage and high capacity, and the so-called lithium secondary battery using the organic electrolytic solution which consists of an organic-solvent solution of lithium salt as nonaqueous electrolyte, such as chalcogen compounds, for example, manganese dioxide, molybdenum disulfide, selenium-ized titanium, etc., such as the oxide and sulfide of transition metals, and a selenide, is examined as a metal lithium and a positive active material as a negative-electrode active material.

[0003] However, although this lithium secondary battery can choose the intercalation compound in which the charge-and-discharge property was comparatively excellent as a positive active material, the charge-and-discharge property of the metal lithium of a negative electrode is not necessarily excellent. Therefore, it was difficult to lengthen the cycle life which repeats charge and discharge, there was a possibility that generation of heat by the internal short circuit might moreover take place, and the problem was in safety. That is, the metal lithium of a negative-electrode active material is eluted as a lithium ion in the organic electrolytic solution by electric discharge. The eluted lithium ion has some which deposit as an activity shape [shape of arborescence or moss] metallic crystal by charge, without depositing flat and smooth altogether like origin although deposited on a negative-electrode front face as a metal lithium. The front face of the metallic crystal itself is being worn with a passive state coat, and is inactivated, and an activity metallic crystal stops being able to contribute it to electric discharge easily while decomposing the organic solvent in the electrolytic solution. Consequently, since negative-electrode capacity fell as the charge-and-discharge cycle progressed, negative-electrode capacity needed to be made remarkably larger than that of a positive electrode at the time of cell production. Moreover, an activity arborescence metal lithium crystal may penetrate separator, may contact a positive electrode, and may carry out an internal short circuit. By the internal short circuit, a cell has a possibility of generating heat.

[0004] Then, as a negative-electrode material, the so-called rechargeable lithium-ion battery using the carbon material which can repeat an intercalation and a day intercalation in reversible is proposed by charge and electric discharge, research and development is actively done, and the utilization stage is already greeted by them. Since an activity arborescence metal lithium crystal does not deposit on a negative-electrode front face at the time of charge and discharge unless this rechargeable lithium-ion battery is overcharged, improvement in safety can expect very much. Furthermore, since this cell excels remarkably the lithium secondary battery which uses a metal lithium for a negative-electrode active material in the high charge-and-discharge property and the cycle life, the need of this cell is elongated quickly in recent years.

[0005] LiCoO₂ which is equivalent to an electric discharge state as a positive active material of a 4V class rechargeable lithium-ion battery, LiNiO₂, LiMnO₂, and LiMn₂O₄ etc. -- the multiple oxide of a lithium and transition metals is adopted or examined As an electrolyte, nonaqueous electrolyte, such as the organic electrolytic solution and a polymer solid electrolyte, is used like a lithium secondary battery.

[0006] When a graphite is used for negative-electrode material, the theoretical values of the capacity per 1g of carbon on the basis of C₆ Li of the intercalation compound which the intercalation of the lithium ion is carried out and it generates are 372mAh(g). Therefore, in various carbon material, you should choose that to which the theoretical value of this amount of specific volume is approached, and it becomes high as much as possible as a negative electrode of a practical use cell, the capacity value (mAh/cc), i.e., the capacity density, per unit volume.

[0007] In the difficulty graphitized carbon commonly called a hard carbon among various carbon material, the material exceeding said amount theoretical value of specific volume (372 mAh/g) is found out, and examination is advanced. However, the true specific gravity of the amorphous carbon of difficulty graphitization nature is small, and since it is bulky, it is substantially difficult [it] to enlarge capacity density of a negative electrode. It cannot be said as **, so that the negative-electrode potential after charge moreover resembles metal lithium potential, but a discharge potential has many technical problems, like flat nature is also inferior.

[0008] On the other hand, since the potential after charge is approximated to metal lithium potential, and the flat nature of a discharge potential is also excellent and a charge-and-discharge property improves as a practical use cell when a natural graphite with high crystallinity and artificial-graphite powder are used for a negative electrode, recently, graphite system powder is

becoming in use [negative-electrode material].

[0009] It is in it, and if the mean particle diameter of the graphite powder for negative electrodes of a rechargeable lithium-ion battery is large, there is an inclination for the charge-and-discharge property in high rate and the electric discharge property in low temperature to be inferior.

[0010] Then, if a powdered mean particle diameter is made small and a mean particle diameter will be made small too much at ** and others although a high charge-and-discharge property and a low-temperature electric discharge property improve, when a powdered specific surface area becomes large too much, the problem to which the irreversible capacity which the lithium inserted by the initial charge into powder cannot contribute to the electric discharge after the 1st cycle becomes large will arise. While this phenomenon was a fatal fault, when a cell was left to a high-energy density-ized intention under an elevated temperature which exceeds 100 degrees C, it makes the solvent in the organic electrolytic solution disassemble, has a possibility of it not only carrying out self-discharge, but raising cell internal pressure and causing liquid spill accident, and had become the cause of reducing the reliability of a cell.

[0011] From the above thing, a suitable specific surface area and the suitable mean particle diameter for the graphite powder for negative electrodes are importantly understood to be a bird clapper easily. It is indicated that invention proposed from such a viewpoint uses the graphite powder the specific surface area by the BET adsorption method is 1-10m²/g in JP,6-295725,A, and a mean particle diameter is 10-30 micrometers, and either [at least / whose] the content of powder with a particle size of 10 micrometers or less or the content of powder with a particle size of 30 micrometers or more is 10% or less. Furthermore, in JP,7-134988,A, the meso carbon micro bead which heat-treats and generates a petroleum pitch at low temperature is graphitized, the spacing (d002) of the field by the wide angle X-ray diffraction method (002) is 3.36-3.40A, and using the nodular-graphite powder whose specific surface area by the BET adsorption method is 0.7-5.0m²/g is indicated. Moreover, using the polyphase carbon matter with which specific surface area has 1/2 or less specific surface area of the nuclear carbon matter by below 20m² / g in JP,5-307959,A is indicated.

[0012]

[Problem(s) to be Solved by the Invention] Invention mentioned above was effective for the reduction of the irreversible capacity determined in early stages of a cycle which it is not only very effective for improvement in the high charge-and-discharge property of a rechargeable lithium-ion battery, and the electric discharge property at the time of low temperature, but can say that it is fatal. However, to the shelf life and reliability by neglect under an elevated temperature, it is inadequate and the dissatisfaction remained also in respect of the amount (mAh/g) of specific volume of a negative electrode, and capacity density (mAh/cc). this invention sets it as the purpose to aim at the further reliability of a lithium secondary battery, and an improvement of the formation of high-energy density.

[0013]

[Means for Solving the Problem] In order to solve the technical problem in the rechargeable lithium-ion battery mentioned above, this invention (1) Are based on a wide angle X-ray diffraction method. The spacing of a field (002) (d002) by less than 3.37A And the size of the microcrystal of C shaft orientations (Lc) At least 1000A or more (2) to an Ar-ion-laser Raman spectrum The R value which is the peak intensity ratio of 1360cm⁻¹ to the peak intensity of 1580cm⁻¹ which can be set is 0.3 or less. the thickness of the portion with the thinnest 1580cm⁻¹ full width at half maximum whose or less [24cm -] 1 (3) mean particle diameter is 10-30 micrometers Below at least 3-micrometer or more mean particle diameter (4) The X diffraction peak intensity ratio of/(004) according [10.0m² / below g(5) tapping density] in the specific surface area by the BET adsorption method to 0.5g/cc or more 1.0g/cc] or less(6) wide-angle X-ray diffraction method (110) more than 3.5m² / g 0.015 or more properties By using the shown massive graphite powder as a nucleus, calcinating by the 700-2800-degree C temperature requirement under inert gas atmosphere after covering a carbon precursor on the front face of the nucleus, and using the carbonaceous powder of the double layer structure in which the surface of a carbonaceous object was made to form as a negative-electrode material While making small irreversible capacity accepted in an initial cycle as much as possible, the shelf life and reliability of a cell in the neglect under an elevated temperature are improved, the outstanding high-rate-discharge property and the electric discharge property in low temperature are secured, and realization of a nonaqueous electrolyte rechargeable battery with the high amount of specific volume is enabled.

[0014]

[Embodiments of the Invention] Invention of this invention according to claim 1 is equipped with the separator allotted between a positive electrode, a negative electrode, and these. the aforementioned negative electrode As a negative-electrode material into which a lithium ion can repeat an intercalation and a day intercalation in reversible by charge and electric discharge (1) Are based on a wide angle X-ray diffraction method. The spacing of a field (002) (d002) by less than 3.37A And the size of the microcrystal of C shaft orientations (Lc) At least 1000A or more (2) to an Ar-ion-laser Raman spectrum The R value which is the peak intensity ratio of 1360cm⁻¹ to the peak intensity of 1580cm⁻¹ which can be set is 0.3 or less. the thickness of the portion with the thinnest 1580cm⁻¹ full width at half maximum whose or less [24cm -] 1 (3) mean particle diameter is 10-30 micrometers Below at least 3-micrometer or more mean particle diameter (4) The X diffraction peak intensity ratio of/(004) according [10.0m² / below g(5) tapping density] in the specific surface area by the BET adsorption method to 0.5g/cc or more 1.0g/cc] or less(6) wide-angle X-ray diffraction method (110) more than 3.5m² / g 0.015 or more properties The shown massive graphite powder is used as a nucleus. After covering a carbon precursor on the front face of the nucleus, While improving many properties of a rechargeable lithium-ion battery by calcinating by the 700-2800-degree C temperature requirement under inert gas atmosphere, and making it the nonaqueous electrolyte rechargeable battery using the carbonaceous powder of the double layer structure in which the surface of a carbonaceous object was made to form, high-energy

density-ization can be attained.

[0015] The above (1) The massive graphite particle which has the property of - (6) is a high grade, and the natural or artificial shape of a scale and scale-like graphite of high crystallinity Chamfering-trituration and ****-trituration, By collecting what has the large thickness of a graphite powder, i.e., what is close to a globular form also in a scale-like particle, in process of sieving after balling-up trituration, specific surface area is not increased to ** and others, and tapping density can obtain 0.5 or more particles. Moreover, that the X diffraction peak intensity ratio of/(004) by the wide angle X-ray diffraction method (110) at this time indicates 0.015 or more to be is good. Furthermore, it is the degree of mean-circle form (the boundary length of a granular-structure product equivalent circle is used as a molecule, and the boundary length of the picturized particle projection image by the ratio made into the denominator). it is set to 1, so that a particle image is close to a perfect circle, and a particle image is long and slender -- it is -- it is -- such a small value that it is carrying out convexo-concave one -- becoming -- that which is spheroidizing as 0.940 or more and a configuration factor is good Although the method of carrying out chamfering and sifting out after grinding to the shape of a disk and a tablet-like particle is raised, if it is process in which a scale-like graphite particle is further pulverized with a fluid energy grinder as an example and is the graphite particle which shows the physical properties of above-mentioned (1) - (6), especially the creation method will not be limited.

[0016] Although used suitably [10-30 micrometers of mean particle diameters of the above-mentioned graphite powder], 12-26 micrometers is more desirable, and 15-23 micrometers is the most desirable. At this time, when content of the powder which exceeds 10% or less or the particle size of 25 micrometers for the content of powder with a particle size of less than 10 micrometers preferably 20% or less is preferably made into 10% 20% or less, it is still more desirable. Furthermore, respectively, when the content of the powder exceeding the particle size of less than 10 micrometers and the particle size of 25 micrometers reaches 10% or less preferably and considers as 10% or less preferably 20% or less, respectively, it is the most desirable 20% or less. Although the specific surface area by the BET adsorption method can use the thing of the range of 3.5-10.0m² / g, its 4.0-8.0m² / g are desirable, and its 4.0-7.0m² / g are the most desirable.

[0017] The graphite particles which carried out in this way and were selected although the theoretical values of the capacity per 1g of carbon on the basis of C6 Li of the intercalation compound which the intercalation of the lithium ion is carried out and it generates were 372mAh(s) are a charge-and-discharge rate 0.2 mA/cm² Electric capacity measurement by the half cell using the lithium metal counter electrode carried out is performed, and if the amount of specific volume is more preferably close to 350 or more mAh/g and the above-mentioned geometric capacity, it will be suitably used by 330 or more mAh/g of nearer things.

[0018] As a carbon precursor for covering the graphite particle nucleus front face which can be used by this invention, first as the organic substance which advances carbonization by the liquid phase Coal system heavy oil, such as a coal tar pitch from a soft pitch to a hard pitch, and a coal liquid, Petroleum system heavy oil, such as naphtha tar division-into-equal-parts' solution system heavy oil which carries out a byproduction at the time of pyrolysis of direct-current system heavy oil, such as an asphaltene, a crude oil, naphtha, etc., Heat treatment pitches, such as an ethylene tar pitch obtained by heat-treating decomposition system heavy oil, FCC decantation oil, and the Ashland pitch, etc. can be used. Furthermore, it is vinyl system macromolecules, such as a polyvinyl chloride, a polyvinyl acetate, a polyvinyl butyral, and polyvinyl alcohol, and 3. - 3 A methyl phenol formaldehyde resin, 5 - Matter, such as sulfur ring compounds, such as nitrogen ring compounds, such as aromatic hydrocarbons, such as substitution phenol resin, such as a dimethylphenol formaldehyde resin, an acenaphthylene, a deca cyclene, and an anthracene, a phenazine, and an acridine, and a thiophene, is raised. Moreover, a thermosetting resin raw material like thermosetting resin, such as aromatic system polymer, such as chain-like vinyl resin, such as naturally-occurring polymers, such as a cellulose, a polyvinylidene chloride, and a polyacrylonitrile, and a polyphenylene, a furfuryl alcohol resin, phenol-formaldehyde resin, and an imido resin, or furfuryl alcohol as the organic substance which advances carbonization etc. is raised with solid phase. Suitably, by choosing a solvent and carrying out dissolution dilution, these organic substance is made to adhere to the front face of a graphite particle nucleus, and can be used if needed.

[0019] Although the carbonaceous powder of the double layer structure which made the surface of a carbonaceous object form in the front face of a graphite particle nucleus finally by usually heating what mixed this graphite particle nucleus and carbon precursor in the invention in this application, obtaining an intermediate product, carbonization-calcinating and grinding after that is obtained The rate of the carbonaceous object in the carbonaceous powder of a double layer structure is adjusted so that it may become [50 or less % of the weight] 2 % of the weight or more 10 or less % of the weight preferably especially 1% of the weight or more 15 or less % of the weight still more preferably 0.5% of the weight or more 25 or less % of the weight 0.1% of the weight or more.

[0020] The manufacturing process for on the other hand obtaining the double layer carbonaceous object which the invention in this application requires is divided into the following four processes.

[0021] The 1st process graphite particle, a carbon precursor, the process that is further mixed using a mixer, a kneading machine, etc. of various marketing of a solvent if needed, and obtains mixture.

[0022] The process which obtains the intermediate product which heated stirring the aforementioned mixture if needed [2nd process], and removed the solvent.

[0023] The process which heats the 3rd process aforementioned mixture or an intermediate product at 700 degrees C or more 2800 degrees C or less under inert gas atmosphere, such as nitrogen gas, carbon dioxide gas, and argon gas, and obtains the carbonization matter.

[0024] The process which carries out [processing / classification / trituration, a crack,] fine-particles processing of the 4th process aforementioned carbonization matter if needed.

[0025] These the in-process 2nd process and, and the 4th process can be skipped depending on the case, and the 4th process may

be performed before the 3rd process.

[0026] Moreover, as heat-treatment conditions for the 3rd process, heat history temperature conditions are important. Although the temperature minimum changes a little also with the kind of carbon precursor, and its heat histories, it is usually 900 degrees C or more preferably 700 degrees C or more. On the other hand, upper limit temperature can be raised to the temperature which does not have the structure order exceeding the crystal structure of a graphite particle nucleus fundamentally. Therefore, as upper limit temperature of heat treatment, 2800 degrees C or less are usually 2000 degrees C or less and a range with 1500 degrees C or less it is still more desirable and desirable preferably. In such heat treatment conditions, a programming rate, a cooling rate, heat treatment time, etc. can be arbitrarily set up according to the purpose. Moreover, after heat-treating in a low-temperature field comparatively, a temperature up can also be carried out to predetermined temperature. In addition, one set or two or more sets are sufficient as the reaction machine used for this process also at a batch process or continuous system again.

[0027] Thus, the carbonaceous powder material of the double layer structure of the invention in this application in which the surface of a carbonaceous object was made to form It is beyond the nuclear value not to exceed the degree of crystallinity of the graphite material used as a nucleus in the peak intensity ratio R value by Raman spectrum analysis and the value of d002 and Lc which are obtained in the diffraction diagram of X-ray wide angle diffraction, i.e., an R value. d002 value of half-value-width $\Delta 2\theta$ is beyond the nuclear value beyond the nuclear value, and, as for Lc, it is desirable that it is below the nuclear value. As an R value of the carbonaceous powder material of a concrete double layer structure, it is mentioned preferably 1.0 or less [0.01 or more] that it is or more 0.2 0.4 or less range still more preferably, and is [or more 0.05] beyond a nuclear value 0.6 or less [0.1 or more] more preferably 0.8 or less. Moreover, although that whose mean particle diameter is 11-40 micrometers is used suitably, 13-30 micrometers is more desirable, and 16-25 micrometers is the most desirable. At this time, when content of the powder which exceeds 10% or less or the particle size of 25 micrometers for the content of powder with a particle size of less than 10 micrometers preferably 20% or less is preferably made into 10% or less 20% or less, it is still more desirable.

Furthermore, respectively, when the content of the powder exceeding the particle size of less than 10 micrometers and the particle size of 25 micrometers reaches 10% or less preferably and considers as 10% or less preferably 20% or less, respectively, it is the most desirable 20% or less. Moreover, that whose average of the thickness of the thinnest portion of a particle is below 4-micrometer or more mean particle diameter is desirable. furthermore, the specific surface area by the BET adsorption method -- 1.0-5.0m² / g -- more -- desirable -- 1.5-4.0m² / g -- the thing of 2.0-3.5m² / g is used suitably still more preferably Although the tapping density of the carbonaceous powder material of a double layer structure improves further rather than the nucleus graphite material used by carbon covering, it is desirable to control in the range of 0.7-1.2g/cc. The carbonaceous powder included in such a range is mixed with a binder or various additives, and it fabricates so that it can be used as an electrode by methods, such as an application and sticking by pressure, on charge collectors, such as copper and nickel. The density (it is called plate density below) of the active material layer on an electrode is adjusted by rolling out by the monotonous press, the roll press, etc. after it. The capacity per unit volume of a cell can be pulled out to the maximum, without reducing the cell capacity at the time of low-temperature electric discharge of a cell, and a high rate discharge by carrying out to 1.5 or less [1.3 or more] more preferably by making plate density or less into 1.6 more greatly than 1.2 at this time. Thus, the cell constituted combining the created negative electrode and the metal chalcogenide type positive electrode for lithium ion batteries usually used can realize the 4V class high voltage, and its capacity is large, the irreversible capacity accepted in an initial cycle is small, the shelf life and reliability of a cell in the neglect under an elevated temperature are high, and it excels in a high-rate-discharge property and the electric discharge property in low temperature extremely. LixMO₂ (M is one or more sorts of transition metals and x= 0 to 1.2) is suitable, and the chalcogenide type positive electrode in this case is LixCoO₂, LixNiO₂, and LixMn₂O₄ especially. And what replaced a part of those Co(es), nickel, and Mn by elements, such as other transition metals, is suitable.

[0028] Although especially this invention does not limit the electrolytic solution, it is suitable to make into a principal component a chain-like carbonate [such as one or more sorts of annular carbonate, such as the ethylene carbonate and propylene carbonate which are excellent in oxidation resistance and a low-temperature property as a solvent of the electrolytic solution used for the cell using the above-mentioned 4 Class V positive electrode and the negative electrode of this invention, and butylene carbonate, dimethyl carbonate and diethyl carbonate, and ethyl methyl carbonate, / one or more sorts of] mixed solvent. Moreover, other solvents, such as an aliphatic carboxylate and ether, are mixable if needed. a mixing ratio -- a rate -- volume conversion -- annular carbonate -- the solvent whole -- 20 - 80% of range has desirable chain-like carbonate 10 to 90% 15 to 40% especially 5 to 50% especially

[0029] Moreover, when using [class / 3V] the material of low voltage for a positive electrode comparatively, solvents other than the above-mentioned solvent can also be used.

[0030] Lithium salt is used for the solute of these solvents. the lithium salt generally known -- LiClO₄, LiBF₄, LiPF₆, LiAlCl₄, LiSbF₆, LiSCN, LiCl, LiCF₃ SO₃, LiCF₃ CO₂, Li (CF₃ SO₂)₂, LiAsF₆, and LiN (CF₃ SO₂)₂ etc. -- it is

[0031] About selection of a required member, restrictions are not prepared at all on cell composition other than the above.

[0032] The cell using the carbonaceous powder material of the double layer structure in which the surface of the above-mentioned carbonaceous object was made to form as a negative electrode improves high charge/discharge capability ability and the high-rate-discharge performance in low temperature compared with the cell using the carbonaceous powder material of the double layer structure in which the surface of a carbonaceous object was made to form using the graphite particle which does not have the graphite particle or the property of above-mentioned (1) - (6) of not making the surface of a carbonaceous object forming as a negative electrode. Moreover, it is hard to make the organic solvent in the electrolytic solution decompose also under an elevated temperature, and since it becomes that it is hard to carry out elevation of cell internal pressure, the liquid spill accident of the electrolytic solution which was a problem conventionally can be prevented. Moreover, since

specific surface area becomes small by making it the carbonaceous powder of a double layer structure, also under an elevated temperature, it is hard to make the organic solvent in the electrolytic solution decompose, and degradation of the cell performance in an elevated temperature can be made small.

[0033]

[Example] Hereafter, the operation gestalt of this invention is explained in detail using a chart.

[0034] (Measuring method)

(1) About one cc of 2vol% solution of polyoxyethylene (20) sorbitan monolaurate was used for the volume criteria mean-particle-diameter surfactant, this was beforehand mixed to carbonaceous powder, and the volume criteria mean particle diameter (median size) was measured by making ion exchange water into a dispersion medium after an appropriate time with the laser diffraction formula particle-size-distribution plan "LA-700" by Horiba, Ltd.

[0035] (2) After using the screen of 300 micrometers of openings, dropping fine particles in the 20 cc tapping cell and filling up with a cell to the limit, to the screen which a sample penetrates using a tapping density Seishin Enterprise milling volume density measuring instrument "tap DIN sir KYT-3000", tapping which is 10mm of stroke length was performed 1000 times, and the tapping density at that time was measured to it.

[0036] (3) After heating at 350 degrees C as predrying and pouring nitrogen gas for 15 minutes using 8000, it measured by the one AMS[by BET specific surface area measurement Ohkurariken CO., LTD.]-BET method in the phase counter pressure 0.3 by nitrogen gas adsorption.

[0037] (4) To the X diffraction sample, about 15% of X-ray standard high-purity-silicon powder was added, it mixed, the sample cell was stuffed, the CuK alpha rays monochrome-ized with the graphite monochromator were made into the line source, and the wide angle X diffraction curve was measured by the reflective formula differential-gear RAKUTO meter method. Based on the **** method, the size (Lc) of the microcrystal of the spacing (d002) of a field (002) and C shaft orientations was measured for the wide angle X diffraction curve obtained by measurement.

[0038] (5) the Raman assay-date book -- a spectrum -- shrine make -- the Raman spectrum analysis using Ar-ion-laser light with a wavelength of 514.5nm using NR-1800 -- setting -- the intensity IA of the peak PA of a near [1580cm-1], and the intensity IB of the peak PB of the range of 1360cm-1 -- measuring -- the ratio of the intensity -- $R=IB/IA$ was measured Moreover, the half-value width of the peak PA of a near [1580cm-1] was asked for the wave number (cm-1) as a unit. It measured by rotating a cell in a field perpendicular to a laser beam, having filled up the cell with the thing of a powder state by natural fall, and irradiating a laser beam on the sample front face in a cell in manufacture of a sample.

[0039] (6) The average of the thickness in the average carbon-powder end of the thickness of the thinnest portion in the end of a carbon powder searched for the molding object from the SEM image of the pressurization direction and the field cut to parallel, after carrying out pressing of each sample offering graphite powder using metal mold. That is, 100 or more values of the thickness direction of the thinnest portion in the end of a carbon powder were measured, and the average was calculated.

[0040] (7) Using metal mold, the X-ray peak intensity ratio of measurement (110)/(004) of the X-ray peak intensity ratio of (110)/(004) pressurized the end of a carbon powder, fabricated it with a density of about 1.7 g/cc in the shape of a pellet, computed the peak intensity ratio of/(004) obtained by wide angle X diffraction measurement (110), and calculated the average. (004) The diffraction line of a field and a field (110) is a diffraction line in the carbon six membered ring reticulated flat surface of a graphite crystal, and its vertical plane. When there are many scale configurations, compared with the case where there are many graphite particles of the shape of the shape of a disk and a tablet, a graphite particle carries out orientation to a pressurization side and a parallel direction alternatively at the time of pellet creation. Therefore, if a scale-like particle increases compared with the graphite particle of the shape of the shape of a disk, and a tablet (110), a /(004) peak intensity ratio will become small.

[0041] (8) The flow formula particle image analysis apparatus "FPIA-1000" by the measurement **** medical use electronic company of the degree of mean-circle form was used, the graphite particle distributed in water was picturized every [1/] 30 seconds by the CCD camera, and the degree of mean-circle form to all particles was computed by carrying out real-time analysis of the particle image. Ion exchange water was used for the dispersion medium, and polyoxyethylene (20) sorbitan monolaurate was used for the surfactant. the degree of mean-circle form is the ratio which used the boundary length of a particle projected-area equivalent circle as the molecule, and made the denominator the boundary length of the picturized particle projection image, it is set to 1, so that a particle image is close to a perfect circle, and a particle image is long and slender -- it is -- it is -- it becomes such a small value that it is carrying out convexo-concave one

[0042] (Example 1 of a fundamental experiment) Drawing 1 is the cross section of the coin form cell for measuring the reversible capacitance and irreversible capacity of a negative electrode of a rechargeable lithium-ion battery. In drawing 1, spot welding of the grid 3 which becomes the inner base of the cell case 1 made from stainless steel from the expanded metal made from stainless steel is carried out beforehand, and the mixture which makes a principal component the carbon-powder end for negative electrodes of this grid 3 and a rechargeable lithium-ion battery is fixed to one as a carbon electrode 5 by the casting-in can method. The mixture of a carbon electrode 5 mixes the end for a sample offering of a carbon powder, and an acrylic binder by the ratio of 100:5 by the weight ratio. The gasket 7 made from polypropylene is attached in the periphery of the cover 2 made from stainless steel, and the metal lithium 4 is stuck to the inside of a cover 2 by pressure. After making a carbon electrode 5 carry out **** sinking in of the nonaqueous electrolyte, distributor shaft coupling of the cover 2 with gasket 7 is carried out to the cell case 1 through the separator 6 which consists of a microporosity polyethylene film, inboard is made to curl and upper-limb opening of the cell case 1 is obturated. In addition, as nonaqueous electrolyte, the organic electrolytic solution which made the concentration of 1 mol/l dissolve a 6 fluoride [phosphoric-acid] lithium in the mixed solvent of the volume ratio 1:1 of

ethylene carbonate and diethyl carbonate was used. It is current density 0.3 mA/cm² at a 20-degree C basis, using the sample offering carbon-powder end of 14 kinds for a carbon electrode 5, producing a cell, and using a positive electrode and the metal lithium electrode 4 as a negative electrode for a carbon electrode 5. It charges and discharges by the constant current. Let the amount which deintercalated and asked for the lithium from carbon be a reversible capacitance until cell voltage is set to 1.0V, after intercalating a lithium in carbon until cell voltage is set to 0V. The value which ** (ed) the reversible capacitance from quantity of electricity which intercalation took was made into irreversible capacity. In addition, the charge-and-discharge final-voltage value of these test cells is negative-electrode carbon / positive electrode LiCoO₂. It is mostly equivalent to charge final-voltage 4.20V of the practical use cell of a system, and discharge-final-voltage 2.75V.

[0043] tapping density was raised by the scale-like artificial graphite, the natural graphite, and the various trituration methods which grind by the conventional method and are acquired -- as artificial, natural-graphite powder (sample No.1-15), and a comparison sample with them The spherical meso carbon micro bead which graphitized the meso carbon micro bead currently indicated by JP,7-134988,A (it MCMB(s)) Sample No.16 and petroleum-pitch-coke powder (sample No.17) are made into the end for negative electrodes of a sample offering carbon powder, and the physical-properties value of these powder, the reversible capacitance mentioned above, and irreversible capacity are collectively shown in Table 1.

[0044]

[Table 1]

材料	製造元	商品名	粉末物性値										電気特性	
			d002 (Å)	Lc (Å)	ラマン R 値	ラマン 半値幅 (cm ⁻¹)	平均 粒径 (μm)	比表 面積 (m ² /g)	層厚部 平均 厚さ (μm)	タンビ ン度 率 (g/cc)	平均 円形度	(110)/ (004)	可逆 容量 (mAh/g)	不可逆 容量 (mAh/g)
黒鉛	ティムカール	KS15	3.36	1000 以上	0.16	21.1	7.8	14.5	1.1	0.32	0.928	0.008	351	53
黒鉛	ティムカール	KS25	3.36	1000 以上	0.16	21.4	10.1	11.9	1.3	0.40	0.925	0.009	353	43
黒鉛	ティムカール	KS44	3.36	1000 以上	0.15	22.2	18.8	9.3	1.8	0.41	0.919	0.010	359	36
黒鉛	ティムカール	KS75	3.36	1000 以上	0.15	22.2	23.7	7.2	2.1	0.44	0.918	0.011	353	35
黒鉛	日本黒鉛	SP-10	3.35	1000 以上	0.18	21.2	32.5	6.9	2.4	0.41	0.927	0.012	353	32
黒鉛	日本黒鉛	SP-20	3.36	1000 以上	0.15	24.0	14.9	8.7	1.8	0.23	0.937	0.010	356	40
黒鉛	エスイーシー	SNO10	3.35	1000 以上	0.19	20.9	10.4	8.7	2.0	0.46	0.919	0.008	362	39
黒鉛	エスイーシー	SNO15	3.35	1000 以上	0.17	21.5	12.9	7.8	2.3	0.46	0.927	0.009	361	35
黒鉛	エスイーシー	SNO20	3.36	1000 以上	0.16	21.6	18.7	6.8	2.5	0.48	0.930	0.009	358	34
黒鉛	日本黒鉛	ACP-20NB	3.36	1000 以上	0.18	21.6	19.0	4.9	5.4	0.64	0.947	0.038	354	23
黒鉛	日本黒鉛	ASP-20NB	3.36	1000 以上	0.17	21.1	16.7	4.9	6.3	0.66	0.943	0.039	357	20
黒鉛	日本黒鉛	SP-20NB	3.36	1000 以上	0.20	20.9	15.7	6.6	3.5	0.61	0.942	0.032	360	26
黒鉛	中越黒鉛	H-0	3.36	1000 以上	0.21	22.0	22.3	5.6	5.6	0.65	0.940	0.035	358	24
黒鉛	中越黒鉛	H-1	3.36	1000 以上	0.18	21.8	18.4	5.8	6.5	0.79	0.941	0.038	355	24
黒鉛	中越黒鉛	H-2	3.36	1000 以上	0.24	22.1	17.7	6.4	5.8	0.70	0.940	0.039	356	26
黒鉛	大阪ガス	MCMB	3.37	700	0.19	25.4	5.3	2.9	5.3	1.10	0.966	0.120	295	18
黒鉛	日本黒鉛	GMW-20NB	3.37	750	0.32	25.0	17.2	5.3	8.1	0.95	0.961	0.110	298	27

PCL XL error

Subsystem: KERNEL

Error: IllegalOperatorSequence

Operator: SetColorSpace

Position: 3570